



Electrochemical sensor based on reduced graphene oxide/carbon black/chitosan composite for the simultaneous determination of dopamine and paracetamol concentrations in urine samples



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ABSTRACT

A sensor based on glassy carbon electrode (GCE) modified within reduced graphene oxide (RGO) and carbon black (CB) in a chitosan film (CTS) is presented. The combination of the nanomaterials with CTS provided a stable dispersion and could be successfully used as electroactive layer. By using the Nicholson method and the results obtained by cyclic voltammetry with the proposed RGO-CB-CTS/GCE, the heterogeneous electron transfer rate constant (k^0) of $5.6 \times 10^{-3} \text{ cm s}^{-1}$ was obtained. The proposed electrode was applied for the simultaneous determination of dopamine (DA) and paracetamol (PAR). Employing square-wave voltammetry, DA presented an anodic peak at 0.25 V and PAR at 0.50 V vs. Ag/AgCl (3.0 mol L⁻¹ KCl). The analytical curves obtained were linear in the range from 3.2×10^{-6} to $3.2 \times 10^{-5} \text{ mol L}^{-1}$ and from 2.8×10^{-6} to $1.9 \times 10^{-5} \text{ mol L}^{-1}$ for DA and PAR, respectively, with detection limits of 2.0×10^{-7} for DA and $5.3 \times 10^{-8} \text{ mol L}^{-1}$ for PAR. The developed sensor presented advantages such as simple preparation, low cost of the nanomaterials employed and a fast response. Besides, it could successfully apply in the determination of DA and PAR in biological samples.

1. Introduction

During the last years, carbon nanomaterials such as graphene (GR), carbon black (CB), and carbon nanotubes have been attracted scientific and technological interest due to their unique properties, including high surface area, thermal and electrical conductivity, and mechanical strength [1–3], being promising materials for optimization of electronic components [4], fuel cells [5–7], solar cells [8–10], batteries [10–12], sensors and biosensors [13–15].

Since 2004, when Novoselov et al. [16] proposed a mechanism to prepare sheets of GR by exfoliation of pyrolytic graphite, it has become a material widely studied by numerous researchers in various areas, including applications in electroanalysis [17]. GR is a material composed of sp² hybridized carbon atoms in the form of an infinite two-dimensional layer. It presents one of its lateral dimensions in the nano scale, which confers specific physicochemical properties compared to the same material as a solid in the form of graphite (bulk) such as electrocatalytic activity for some reactions.

The main method to obtain graphene was proposed by Hummers and Offeman [18] in which basically is used a mixture of sulfuric acid, sodium nitrate and potassium permanganate. The graphite has a layered structure with an approximate spacing of 3.35 Å between its layers (also called sheets) [19]. The exfoliation of graphite oxide can occur under moderate ultrasonication, for example, and as result is obtained a few individually sheets that are denominated graphene oxide (GO). An attractive characteristic of this material is that it can be reduced to graphene sheets. When this happens some oxygenated groups in GO can be removed and conjugated structures arise. For this purpose, some reducing agents are used such as e.g., hydrazine [20], ascorbic acid [21], or sodium borohydride [22]. This type of GR is known as reduced graphene oxide (RGO), which is a hydrophilic material as compared to the GR (hydrophobic). Besides, its structure is composed mostly by sp² hybridized carbons, which contributes for a higher conductivity compared to GO (most carbons are sp³) and become an interesting material in the development of electrochemical sensors.

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CB is an amorphous carbon nanomaterial, which is composed mostly of sp^2 hybridized carbons and a few sp^3 carbons atoms. Its particles are arranged into reticulate chains or branches, in which are observed a graphite-like crystal composition. It has attracted attention of scientists for several reasons such as high ratio of surface area and volume, low cost and ability to produce a stable dispersion in aqueous and organic solutions without the use of sophisticated preparations [23,24]. To present these interesting properties CB and RGO have been extensively applied to modify electrode surfaces to construct new architectures of sensors [23,25–27] for the determination of different analytes e.g., pesticides [28,29], phenolic compounds [30,31], heavy metals [32,33], and drugs [24,34–36].

Sometimes, with the purpose to obtain a homogenous and stable dispersion with carbon materials are used some substances (surfactants, polymers and others) such as dihexadecyl hydrogen phosphate [37,38], polyallylamine hydrochloride [39], poly(ethylenimine) [40], poly(sodium styrenesulfonate) [41] and chitosan (CTS) [42]. They can interact in aqueous or organic medium, and when this dispersion is deposited on the electrode there is the formation of a thin film. It is expected that this film present adhesion on the working electrode and promote a great transfer electron transfer between the electrode/solution interface.

Dopamine (DA) is an important neurotransmitter (related to nerve cells sending signals and commands to other nerve cells) [43] in the human body whose low concentration or dysfunction may be associated with some important diseases such as Parkinson [44]. On the other hand, paracetamol (PAR), also known as acetaminophen, is one of the most popular drug used to relieve chronic pain and, due to its anti-inflammatory activity, it can be combined with other opioid analgesics to promote the relief of severe pain after surgeries [45]. One of the aggravating symptoms of the Parkinson disease is the loss of control of motor function leading the patient to constant chronic pain. So, to relieve this pain, some doctors prescribe for the patient different painkillers, including the PAR, and thus we are able to find together the DA and the PAR in the urine excreted by the carrier of the disease. In this context, it is important to quantify these analytes individually and to verify if one of them interfere with quantification of another when found together in the same sample, and, for this purpose, it necessary to propose sensitive methods for the simultaneous determination of DA and PAR concentrations [46,47].

In this work, we report for the first time a new sensor using RGO and CB within CTS film on the glassy carbon electrode (GCE) denoted as RGO-CB-CTS/GCE. The synergistic effects of dispersion RGO-CB were well done available comparing with GCE modify only with RGO and CB. As result, the RGO-CB-CTS/GCE displays a selective electrocatalytic oxidation towards DA and PA, presenting to be an economical device with fast response and easy to construct for simultaneous determination of DA and PAR in biological samples.

2. Experimental

2.1. Chemicals

Sodium borohydride, NH_3 , HCl, DA, PAR, CTS of low molar mass (degree of deacetylation of 80%), urea, glucose, ascorbic acid, uric acid and potassium ferricyanide graphite powder were obtained from Sigma-Aldrich, expanded graphite was donated from National graphite, Brazil. The VXC72R carbon black was kindly supplied by Cabot Corporation. All other reagents were of analytical grade. All solutions were prepared with ultrapure water (resistivity $\geq 18.0 M\Omega cm$) obtained from a Millipore Milli-Q system (Billerica, USA). $0.1 mol L^{-1}$ phosphate buffer solution (pH 6.2) was used as supporting electrolyte, prepared with Na_2HPO_4 and NaH_2PO_4 salts obtained from Sigma-Aldrich.

A stock solution of 1.0% m/v CTS was prepared by dissolving 100 mg of CTS powder in 10 mL of 1.0% (v/v) acetic acid solution. The mixture was vigorously stirred for 3 h until complete dissolution, and

then was stored under refrigeration at $4^\circ C$ [42].

Stock solutions containing $1.0 \times 10^{-2} mol L^{-1}$ DA and PAR were prepared by dissolving both substances in $0.1 mol L^{-1}$ phosphate buffer solution (pH 7.0). When necessary, standard solutions were prepared at different concentrations by dilutions of the stock solution.

2.2. Instruments

Scanning electron microscopy (SEM) images of RGO were obtained with FEG XL30 (Philips®). A Hitachi U2001 spectrometer was used for measurements of Ultraviolet spectroscopy of RGO. It was also employed an infrared spectrometer Fourier transform (FTIR) Nicolet iS50 (Thermo Scientific) to verify the presence of functional groups in the GO and RGO and a dynamic light scattering Zetasizer Nano ZS90 (Malvern) was used to estimate the average diameter of the RGO sheets size.

Electrochemical measurements were performed by using an Autolab PGSTAT12 (Metrohm-Autolab) potentiostat/galvanostat coupled to a microcomputer managed by 4.9 GPES software. A 10 mL conventional three-electrode system, using the sensor RGO-CB-CTS/GCE as working electrode, a platinum plate as a counter electrode, and an Ag/AgCl ($3.0 mol L^{-1}$ KCl) as a reference electrode were employed for electrochemical studied. In addition, all measurements were performed at room temperature ($25 \pm 1^\circ C$). The pH measurements were carried out by using a pH meter Orion model EA 940 connected to a combined electrode Digimed glass with a reference electrode Ag/AgCl ($3.0 mol L^{-1}$ KCl).

2.3. Synthesis of reduced graphene oxide and preparation of the proposed electrode

The procedure of RGO synthesis is illustrated in Fig. 1. Initially, GO was synthesized from the graphite powder by the modified Hummer method [18,48,49] (step 1).

After the chemical exfoliation of the graphite (step 2), a viscous solution (dark coloring) was formed, which was left in a dialysis membrane (10 kDa) to remove possible traces of metal cations and other contaminants for two weeks, followed by storage at $4^\circ C$ [22] (step 3), to prevent fungi proliferation.

To reduce 50 mg of GO, it was added 100 mL of dimethylformamide (DMF) and 1 mL of NH_3 (28% v/v) in a 125 mL round-bottom flask and sonicated in an ultrasonic bath for 2 h (step 4). Sequentially, the resultant mixture was left in reflux at a temperature of $95^\circ C$. After achieved this temperature we added $0.1 mol L^{-1}$ sodium borohydride to the mixture (step 5). GO reduction occurred for 8 h. To remove DMF, the solution remained one week in a dialysis membrane (10 kDa) and the solvent DMF was changed by water (concentration final of RGO was $0.8 mg mL^{-1}$) (step 6). The dispersion was stored in a glass flask at $4^\circ C$.

Glassy carbon electrode (GCE) ($\varnothing = 3.0 mm$) was polished with $0.5 \mu m$ alumina for 5 min to obtain a mirror-like surface on the electrode and then washed with ultrapure water every day before measurements. An aliquot of 600 μL of RGO stock solution was mixed with 0.5 mg of CB and 400 μL of CTS (from stock solution) to form a stable dispersion. This suspension was transferred to an ultrasonic bath for 30 min, then, 8 μL of the RGO-CB-CTS dispersion was cast on the GCE surface and the solvent was evaporated at room temperature ($25^\circ C$) for 2 h (step 7). The proposed sensor was named as RGO-CB-CTS/GCE and its schematic fabrication can be seen in Fig. 1.

2.4. Preparation of synthetic urine sample

The synthetic urine samples was prepared as described in the literature [50,51] containing the following chemical compounds: $CaCl_2 \cdot 2H_2O$ (0.28 g), NaCl (0.73 g), Na_2SO_4 (0.56 g), KH_2PO_4 (0.35 g), KCl (0.40 g), NH_4Cl (0.25 g) and urea (6.25 g). All reagents were

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